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Fabrication of Ba-Doped ZnO/PVDF Composite Films for Piezoelectric Energy Conversion Applications

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Abstract

As the need for renewable energy continues to increase, recent years have seen major developments in energy-harvesting methods. These piezoelectric devices work by converting mechanical energy from the surroundings into electrical energy. Here, we focus on enhancing the energy output voltage of piezoelectric materials using various techniques.We synthesized Ba-doped ZnO (BaZ) powders through the co-precipitation process, calcination of powder at 500°C. The prepared ceramic powders exhibited phase formation, as confirmed by X-ray diffraction (XRD). Flexible composite films were fabricated by incorporating calcined Ba-doped ZnO particles into PVDF at a filler concentration of 5 wt.%. The films, produced using the drop-casting technique, had an average thickness of around 60 µm. The structural properties of the fabricated films were characterized by X-ray diffraction, and their surface morphology was investigated using Scanning Electron Microscopy (SEM). To evaluate energy harvesting capabilities, the devices were subjected to mechanical excitation via a shaker, and the resulting voltage output was recorded through the films' electrical contacts. The measured output voltages were 6.32V and 24.6V for PVDFand 5 wt.% CaZ-PVDF films, respectively. These voltage outputs demonstrate the capability of the fabricated films to power small electronic devices.

Introduction

Harvesting energy from various renewable sources, including solar, tidal, thermal, chemical, and mechanical energy from the environment, has garnered significant attention as a means to address critical global challenges such as the rapid depletion of fossil fuels, global warming, and energy crises. [1, 2]. Mechanical energy is considered one of the most widespread, readily available, and abundant renewable sources. Different methods have been investigated to capture it, including triboelectric effects, electromagnetic induction, and piezoelectric conversion. Among these, the piezoelectric approach is particularly appealing due to its ability to generate high output energy [3,4]. The electroactive semicrystalline homopolymer poly(vinylidene fluoride) (PVDF), composed of the repeating unit –(CH_2–CF_2)–, together with its copolymers including P(VDF-TrFE), PVDF-HFP, and P(VDF-TrFE-CFE), demonstrates remarkable piezoelectric, pyroelectric, and ferroelectric behaviours. These materials also offer good thermal stability and chemical resistance, making them ideal candidates for the aforementioned applications [5-7]. The semicrystalline nature of PVDF allows it to exist in different crystalline phases, namely α, β, γ, δ, and ε, with α, β, and γ occurring most frequently. The α-phase, defined by a TGTG′ (trans–gauche+–gauche−) arrangement, and the γ-phase, characterised by a TTTGTTG′ chain sequence, possess lower piezoelectric performance in contrast to the β-phase. The β-phase, with its all-trans (TTTT) conformation, exhibits the highest spontaneous polarization, making it the most piezo-electrically active [8, 9]. Zinc oxide (ZnO), a wide bandgap n-type semiconductor, is frequently incorporated into composite films to boost their dielectric and ferroelectric characteristics. Nevertheless, increasing the filler concentration may reduce the inherent flexibility of polymer matrices. To address this, reducing the nano-filler content while achieving improved properties—either through ionic doping or by combining ZnO with other fillersis considered a more effective approach to preserving the polymeric characteristics of composite films[10-13]. Studies indicate that incorporating Ba into ZnO nanoparticles significantly boosts their dielectric constant and high-temperature ferroelectricity. Since Ba^{2+} (1.35 Å) is about 1.8 times larger than Zn^{2+} (0.74 Å), this ionic size disparity generates local dipoles within the lattice. Consequently, Ba doping in the ZnO matrix is anticipated to enhance its piezoelectric properties. Numerous investigations have explored the structural, optical, dielectric, ferroelectric, photocatalytic, magnetic, and gas-sensing properties of barium-substituted ZnO nanoparticles [14-20].

Experimental Section

1. Preparation of Mn-Doped ZnO Ceramic Powder

A simple co-precipitation method was employed to synthesize Ba-doped ZnO (BaZ) ceramic powder [21]. For this synthesis, Barium Chloride and Zinc Chlorideprecursors were used for Barium and zinc, respectively. The precursors were dissolved in distilled water at room temperature and stirred continuously for 2hours using a magnetic stirrer to form a homogeneous solution [22]. Subsequently, sodium hydroxide (NaOH) solution, acting as a strong base, was added slowly into the mixture to promote the formation of precipitates. The mixture was allowed to stand without agitation until the precipitates fully settled at the base of the beaker. The precipitates were then thoroughly washed several times using ethanol and distilled water to ensure purity. He clean precipitates were oven-dried at 90°C for 12 hours and later calcined at 500°C for 2 hours in a muffle furnace, yielding BaZ ceramic powder.

2. Preparation of flexible composite films consisting of BaZ/PVDF

Polyvinylidene fluoride (PVDF), BaZ powder, and N, N-dimethylformamide (DMF) were used to produce flexible composite films. Firstly, DMF and PVDF powder were mixed continuously on magnetic stirring for 1 hour at 40 °C, yielding a clear and homogeneous solution. In a separate step, BaZ powder, pre-calcined at the desired 5 wt.% concentration, was dispersed in DMF and ultra-sonicated until all the particles broke into powder form. The resulting BaZ suspensions (5 wt.%) were then blended with the PVDF solution and stirred magnetically at 45 °C for 2 hours to achieve uniform dispersion. The homogeneous mixture was drop-cast onto a clean glass substrate and subsequently dried in an oven at 80 °C for 1 hour. This process yielded a flexible BaZ/PVDF composite film on the substrate, which could be easily peeled off. All synthesis steps were performed under ambient air conditions, and electrical connections were established using copper wires.

Result and Discussion

1. Structure Analysis of the Composition of BaZCeramic Powder

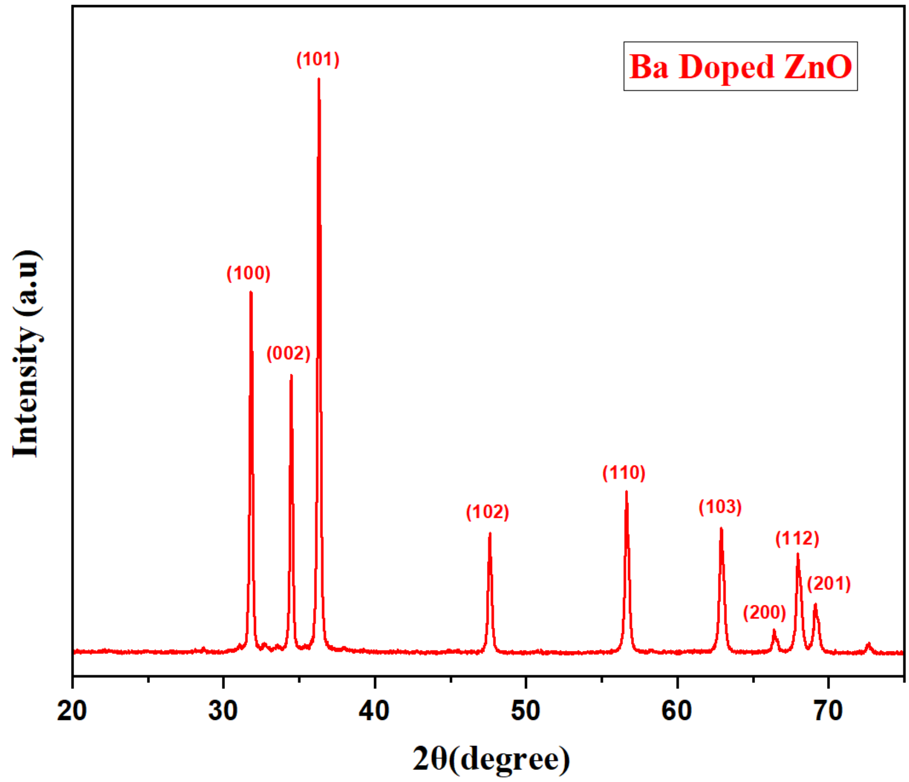

Fig.1 XRD Analysis of BaZ Ceramic Powder.

XRD profiles of Ba-doped ZnO (BaZ) particles are displayed in Fig. 1. As a wide-bandgap semiconductor, ZnO generally adopts wurtzite or zinc blende crystal structures. The wurtzite structure of ZnO is characterized by two polar surfaces, consisting of Zn and O, which create a dipole moment and spontaneous polarization along the c-axis, giving ZnO its piezoelectric properties [23]. The observed peaks closely match the pure ZnO crystalline structure listed in the JCPDS database (card number: 361451), confirming the hexagonal wurtzite phase of ZnO [24]. The introduction of Barium as a dopant causes no significant changes in the diffraction pattern, suggesting that Ba^{2+} ions replace Zn^{2+} ions within the lattice while preserving the hexagonal wurtzite structure. The absence of additional peaks supports this conclusion. However, the lower diffraction peak intensity in BaZ nanoparticles compared to ZnO suggests the successful incorporation of Ba dopant ions in place of Zn ions [25].

2. XRD and SEM Analysis of 0 and 5 wt. % BaZ/ PVDF Composite Films

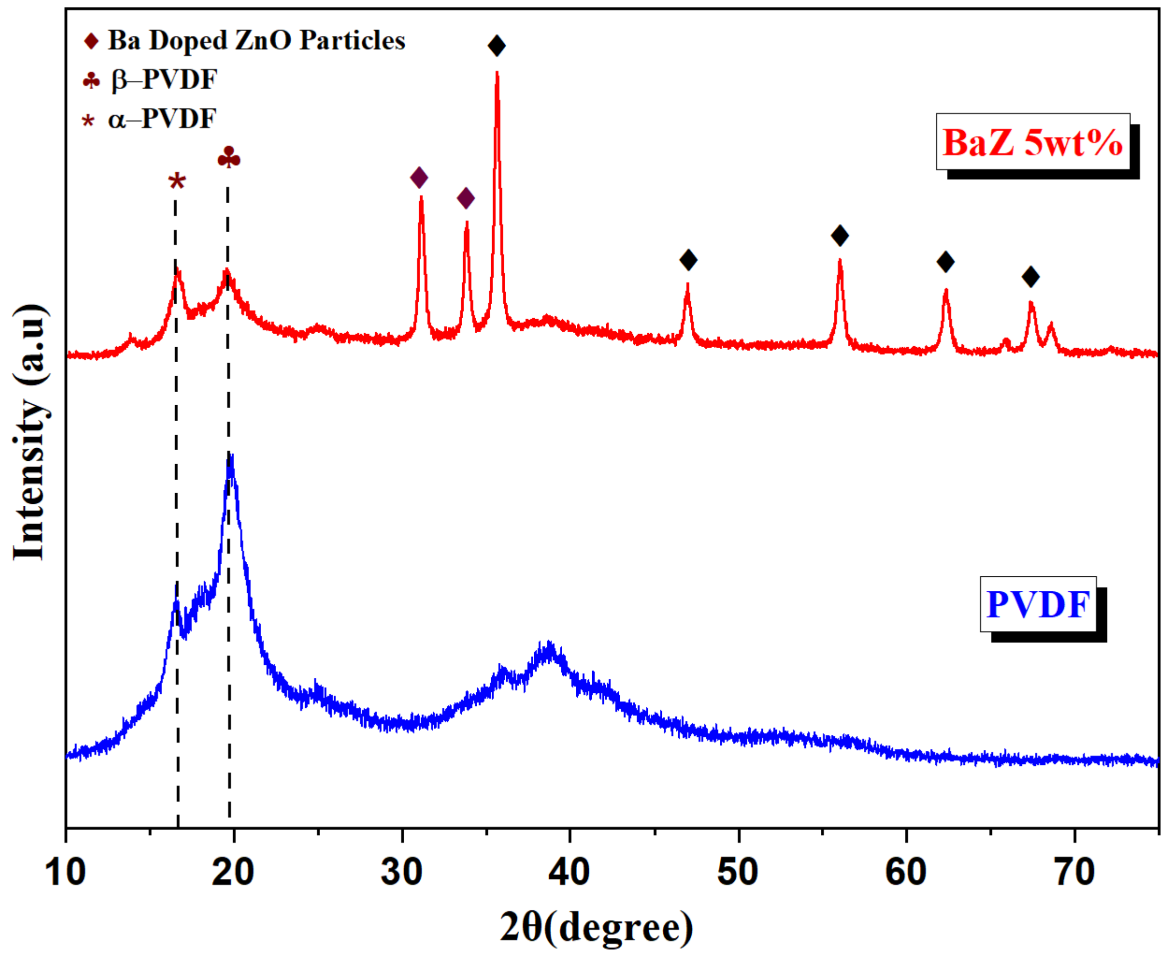

Fig. 2 XRD plots of both pure PVDF and BaZ/PVDF composite film.

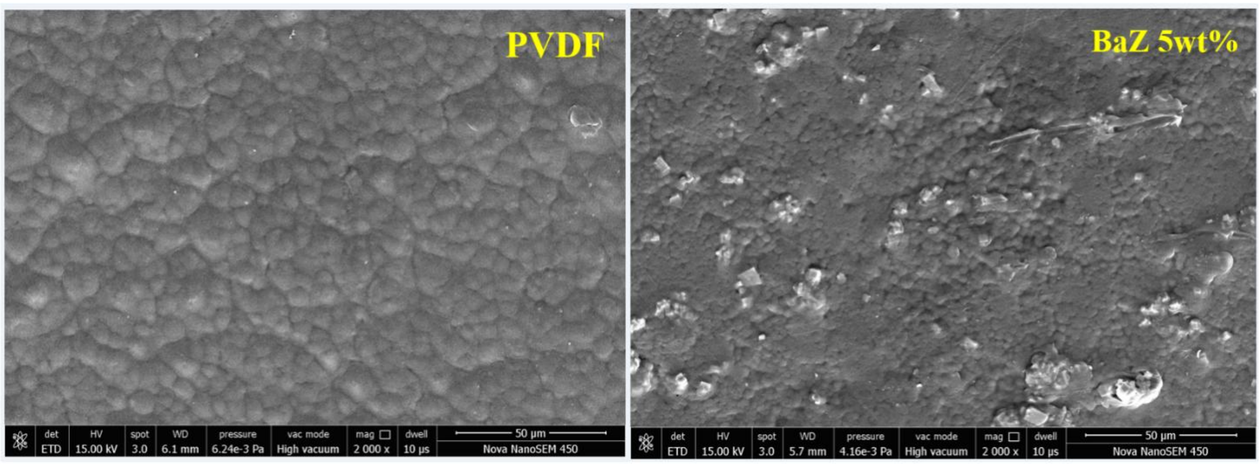

Fig. 3 SEM images of PVDF and BaZ/PVDF composite film.

XRD plots of 0 and 5 wt.% BaZ/PVDF flexible composite films are displayed in Fig. 2. In all the films, a diffraction peak at 20° corresponds to the electroactive polar β-phase of

PVDF, while a broad diffraction peak at 18.0° indicates the presence of the non-polar α-phase in the films [26]. It is visible from the XRD peaksthatBaZ particles intensify as their concentration in the PVDF matrix reaches 5 wt. %. The SEM images in Fig. 3 illustrate the surface morphology of both 0 and 5 wt. % of BaZ flexible composite films, confirming that BaZ particles are evenly embedded throughout the PVDF matrix. This even distribution of BaZ particles facilitates the alignment of dipoles in a specific direction and promotes the efficient movement of charges within the composite film, thereby enhancing the device's performance [27, 28].

Piezoelectric Voltage Output from the PEG Device.

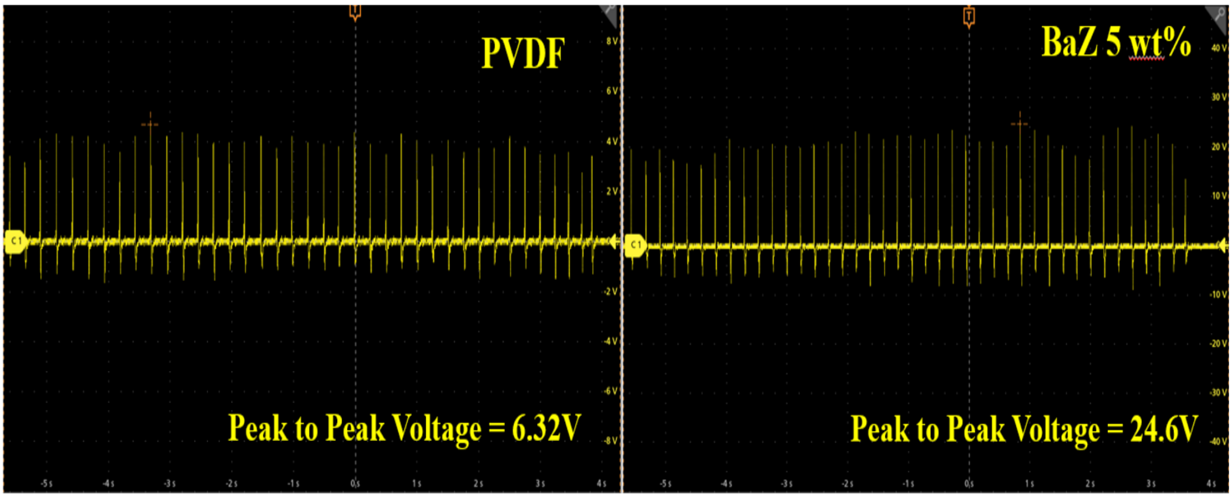

Fig. 4 Voltage output of the (a) PVDF (b) 5 wt.% BaZ PEG Device

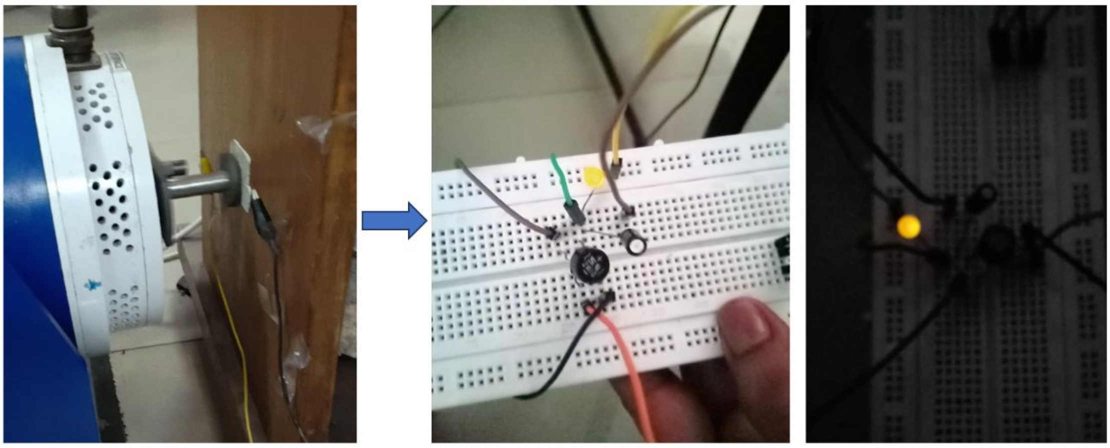

Fig. 5 Shows Application by Glowing LED Light.

Fig. 4 illustrates the voltage responses of two devices: one fabricated from pure PVDF and the other incorporating a BaZ/PVDF composite film. Incorporation of BaZ fillers in the composite PEG device notably improved the produced voltage output relative to the 0 wt. % PEG device. The maximum voltage generated was 24.6 V of 5 wt. % of BaZ, and 6.32 V for pure and 0 wt. % PVDF PEG. This voltage generation results from the deformation of the film's crystal structure under applied stress, which leads to the alignment of electric dipoles [29,30].Fig. 5 shows the energy harvesting application by glowing LED light from the PEG device manufactured from BaZ/ PVDF composite film.

Conclusion

We synthesizedBaZ powder and confirmed its structure using XRD analysis. The composite films, produced by solvent casting, were subsequently characterized by XRD to evaluate their crystalline nature. Findings reveal that the addition of BaZ aids in the emergence of the polar electroactive phase, resulting to increased filler crystallinity. Moreover, embedding BaZ within the PVDF matrix modifies the device behaviour and enhances its piezoelectric response. Under mechanical excitation from a shaker, the voltage output of the BaZ/PVDF PEG reached a maximum of 24.6 V.

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